QUALITY ASSURANCE PROJECT PLAN

FOR

SALTON SEA NUTRIENT WATER QUALITY MONITORING

Prepared by and for
California Regional Water Quality Control Board Staff
Colorado River Basin Region

APRIL 2002

Quality Assurance Project Plan
Salton Sea Nutrient Water Quality Monitoring

APPROVALS:

California Regional Water Quality Control Board

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1 PROJECT MANAGEMENT

1.1 INTRODUCTION

The Porter-Cologne Water Quality Control Act (Porter-Cologne) is the principal law governing water quality regulation in California. This statute established the State Water Resources Control Board (SWRCB) and nine Regional Water Quality Control Boards (RWQCBs), which are charged with implementing its provisions. Porter-Cologne establishes a comprehensive program for the protection of water quality and the beneficial uses of water.

Staff from the California Regional Water Quality Control Board, Colorado River Basin Region (Regional Board), will determine whether discharges in the vicinity of the Salton Sea are adversely impacting water quality of the lake. The Regional Board is the lead agency on this project. Specifically, this investigation focuses on Salton Sea surface water quality from the outflow of the Coachella Valley Water District and the Imperial Irrigation District drain systems, and the Alamo and New Rivers. This Quality Assurance Project Plan (QAPP) is subject to approval by Regional Board staff.

This QAPP follows the format that the U.S. Environmental Protection Agency (USEPA) established in its *Requirements for Quality Assurance Project Plans for Environmental Data Operations, EPA QA/R-5, March 2001*. This QAPP also complies with quality assurance/quality control (QA/QC) procedures of the SWRCB Quality Assurance Program Plan (State Water Resources Control Board 1994). This QAPP describes the quality assurance (QA) and quality control (QC) procedures associated with monitoring activities to characterize impacts of aforementioned discharges on the Salton Sea.

The Quality Assurance Officer is responsible for ensuring that QAPP commitments are implemented and followed to meet project objectives. The Quality Assurance Officer will be independent from the units generating data for this project. The Quality Assurance Officer may, upon mutual concurrence, request modification of this QAPP by the project manager. The QAPP modification process consists of incorporating necessary changes into the QAPP document, obtaining approval signatures, and distributing the revised document to project personnel.

1.2 PROJECT TASK ORGANIZATION

Specific project responsibilities of the Regional Board staff are outlined below. A project organization chart is in Appendix I.

Jose Angel, Project Supervisor, Supervising WRC Engineer, 760-776-8932

- Review and approve the QAPP and subsequent revisions.
- The primary decision maker, responsible for oversight of the project at Regional Board level.

Doug Wylie, Project Manager, Senior WRC Engineer, 760-346-6585

- Review and approve the QAPP and subsequent revisions.
- Ensure that the QAPP is implemented and followed to meet the project objectives.
- Review reports and ensure plans are implemented according to schedule.
- Conduct Health and Safety briefing for sampling team prior to each sampling event.
- Coordinate field and laboratory activities.
- Conduct project activities in accordance with the QAPP.
- Report to the Quality Assurance Officer and management regarding the project status. Prepare

interim and final reports for the Quality Assurance Officer and management.

Maria de la Paz Carpio-Obeso, Quality Assurance Officer, Environmental Scientist, 760-674-0803
- Review and approve the QAPP and subsequent revisions.
- Ensure that the QAPP is implemented and followed to meet the project objectives.
- Review reports and ensure plans are implemented according to schedule.
- Responsible for operation of the Regional Board Laboratory.
- Responsible for coordinating lab quality assurance activities.

Jeff Allred, Field Lead Person, WRC Engineer, 760-776-8946
- Responsible for maintaining and calibrating instruments in the field.
- Responsible for coordinating filed activities and ensuring they are consistent with QAPP.
- Assist with monitoring activities as required.
- Prepare a narrative report on sampling event for the Project Manager.
- Responsible for delivery of samples to the laboratory.
- Responsible for decontamination of sampling equipment used in field.

Nadim Zeywar, Field Sampler, Environmental Scientist, 760-776-8971
- Assist with monitoring activities as required.
- Prepare the Quality Assurance Project Plan (QAPP) and revisions.
- Responsible for processing data, maintaining the project database, and validating the field data.

Jason Voskanian, Field Sampler, SETT, 760-776-8930
- Assist with sampling activities as required.
- Responsible for delivery of samples to the laboratory.

Phan Le, WRC Engineer, 760-346-7491
- Assist with sampling activities as required.
- Responsible for calibration of metering equipment prior to sampling event.
- Responsible for assisting Lab Director with water quality analysis.

Jon Rokke, Field Sampler, WRCE, 760-776-8959.
- Assist with sampling activities as required.
- Responsible for delivery of samples to the laboratory.

Kola Olatunbosun, Field Sampler, WRCE, 760-776-8986
- Assist with sampling activities as required.
- Responsible for delivery of samples to the laboratory.

Theresa Illare, Field Sampler, Environmental Scientist, 760-776-8971
- Assist with sampling activities as required.
- Responsible for delivery of samples to the laboratory.

Maribel Rodriguez, Field Sampler, SETT, 760-776-8971
- Assist with sampling activities as required.

Jose Cortez, Field Sampler, WRC Engineer, 760-674-8142
- Assist with sampling activities as required.

Logan Raub, Field Sampler, Environmental Scientist, 760-776-8966

- Assist with sampling activities as required.

Ivory Reyburn, Field Sampler, Environmental Scientist, 760-776-8933

- Assist with sampling activities as required.

1.3 PROBLEM DEFINITION/BACKGROUND

The Salton Sea Transboundary Watershed is located in southeastern California in the Colorado Desert region of the Sonoran Desert. This watershed drains approximately 8,360 square miles and contains five main surface water bodies: the Salton Sea, Alamo River, New River, Imperial Valley agricultural drains, and Coachella Valley storm water channel (Whitewater River channel).

Pursuant to Section 303(d) of the Clean Water Act (CWA), the Regional Board is developing a nutrient Total Maximum Daily Load (TMDL) for the Salton Sea. This TMDL is being developed because the Region's 303(d) list of impaired water bodies identifies the Salton Sea as water quality limited, in part, because nutrient (biostimulatory substance) concentrations violate the water quality objectives (WQOs) established by the Regional Board to protect the following Salton Sea beneficial uses: aquaculture; warm freshwater habitat; wildlife habitat; preservation of rare, threatened, or endangered species; water contact recreation; non-contact water recreation; and potential industrial service supply. Other violated WQOs include aesthetic qualities, dissolved oxygen, biostimulatory substances, and turbidity.

The Alamo and New Rivers transport agricultural discharge and municipal effluent from the Imperial Valley to the Salton Sea. In addition, the New River transports municipal and industrial effluent from Mexicali, Mexico. The Whitewater River transports agricultural discharges, and municipal and industrial effluent, from the Coachella Valley. In addition, agricultural drains discharging directly to the Sea are an important source of pollutants.

The Salton Sea is classified as a eutrophic lake – impaired by nutrients, which result in low dissolved oxygen, high ammonia and phosphorus levels, algal blooms, and foul odors. The Salton Sea is a federal (since 1924) and state (since 1968) designated repository for agricultural, surface, and subsurface drainage waters from the Imperial and Coachella Valleys. Over 70% of freshwater inflows to the Sea consist of agricultural drain water from Imperial Valley. Because the Sea has no outlet and an evaporation rate of 152 cm/year, salts concentrate in it and nutrients enhance the formation of eutrophic conditions.

Great concern has been expressed about the Salton Sea's increasing salinity, contamination from agricultural and urban sources, algal blooms, and disease outbreaks and large die-offs of fish and waterbirds between 1992 and the present date. Concern has increased due to the importance of the Salton Sea ecosystem to the Pacific Flyway and endangered species.

Therefore, the Regional Board staff is developing a monitoring program to quantify the loads of nutrients to the Salton Sea. This estimation will be included into the TMDL for the Salton Sea.

1.4 PROJECT/TASK DESCRIPTION

Water samples will be analyzed by the laboratory for orthophosphates, total phosphorus, nitrate, nitrite,

ammonia, total nitrogen, total organic carbon, calcium carbonate (hardness), alkalinity, sulfate, biological oxygen demand, chemical oxygen demand, chlorophyll A, total suspended solids (TSS), and turbidity. Field measurements will be made for temperature, pH, dissolved oxygen (DO), electrical conductivity (EC), redox potential, and water flow.

The project consists of monthly sampling events for a minimum of 24 months. During each of these sampling events, water samples will be collected from forty seven (47) monitoring stations, as described in Section 2.1, below. Data from the sampling events, in addition to previously collected data, will be assessed by the project's Quality Assurance Officer based on the results of quality control activities such as analysis of quality control samples and adherence to quality control procedures in the collection and storage of samples. The Project Manager will maintain organized records containing all original sample documentation, such as field notes, chain of custody forms, and laboratory analysis results.

1.5 DATA QUALITY OBJECTIVES AND CRITERIA

The mission of the Regional Board is to preserve and enhance the water quality in the Region for the benefit of present and future generations. With this concept in mind, the Regional Board will ensure that beneficial uses of water bodies within the Region are protected as required by State and Federal laws; this implies that regulatory actions will be taken if a pollution source is identified.

The Water Quality Control Plan for the Colorado River Basin Region (Basin Plan) established water quality objectives that will protect beneficial uses of its water bodies, in this case the Salton Sea. The quality of data obtained for this project should support a determination of whether contributing streams in the Salton Sea are degrading water quality in the lake (source analysis). To determine the extent to which discharges of nutrients from rivers and agricultural drains are impacting the Salton Sea, Regional Board staff will collect water samples and monitor water quality at the outflow of the main rivers and agricultural drains for key indicator parameters. Monitoring stations were chosen based on best professional judgment, locations of contributing streams, previous sampling results, direction of flow in the lake, inflows, and site safety and accessibility.

The Regional Board also will use the data for water quality control planning. In turn, this information may be used by the Regional Board for the recommendation/implementation of infrastructure projects that would result in the elimination of pollution caused by the contributing inflows.

As indicated in Section 1.4, the purpose of this project is to determine the amount and sources of nutrient loading to the Salton Sea. As a result, special attention will be placed on the interpretation of the laboratory nutrient analysis.

Because of these data quality needs, strict adherence to holding times, bottle and preservation requirements, collection techniques, and analytical methodology as stated in the published methods and within the contents of this document is necessary. Data quality objectives for all of the measured parameters are listed in Table No. 1 below. Data Quality Indicators are discussed in Section 1.4.1.

Table 1: QA Objectives for all Measured Parameters

Parameter	Matrix	Units	Precision (RPD)	Accuracy (% Recovery)	Completeness[1] (% C)
Orthophosphate	Water	mg/L	20	80-120	95
Total Phosphorus	Water	mg/L	20	80-120	95
Ammonia	Water	mg/L	20	80-120	95
Nitrate	Water	mg/L	20	80-120	95
Nitrite	Water	mg/L	20	80-120	95
Total Kjeldahl Nitrogen	Water	mg/L	20	80-120	95
Total Organic Carbon	Water	mg/L	20	N/A	95
Hardness	Water	mg/L	20	N/A	95
Alkalinity	Water	mg/L	20	N/A	95
Sulfate	Water	mg/L	20	80-120	95
Total Suspended Solids	Water	mg/L	20	80-120	95
Biological Oxygen Demand	Water	mg/L	20	80-120	95
Chemical Oxygen Demand	Water	mg/L	20	80-120	95
Turbidity	Water	mg/L	20	80-120	95
Temperature	Water	^{o}C	N/A	± 0.15	95
PH	Water	N/A	N/A	± 0.2	95
Dissolved Oxygen	Water	mg/L	N/A	0-200% air saturation: ± 2% of reading or 2% of air saturation[1] 200-500% air saturation: ± 6% of reading	95
Electrical Conductivity (EC)	Water	μmhos/cm	N/A	± 0.5% + 0.001 mS/cm	95
Redox Potential	Water	Eh system	N/A	± 20 mV	95
Chlorophyll A	Water	ug/L Chl.	N/A	N/A	95
Water flow	Water	Cfs	N/A	N/A	95

[1] Completeness criteria will not be applied to results from QC samples.

1.5.1 DATA QUALITY INDICATORS

Precision

The degree of refinement of a measurement will be assessed as the relative percent difference (RPD) for laboratory duplicate samples and field duplicates.

$$RPD = \frac{(C1 - C2)*100}{\left(\frac{C1 + C2}{2}\right)}$$

RPD = relative percent difference
C_1 = larger of the reported value or measurement
C_2 = smaller of the reported value or measurement

Standard deviation will be used if precision is calculated from more than 3 replicates.

Accuracy

Degree of conformity of a measurement to the actual value or standard will be determined by using spiked samples for inorganics. Samples marked QA/QC will be submitted to the current laboratory contractor to evaluate any matrix effects. The samples will be analyzed for ammonia and nitrates, spiked, and reanalyzed. The percent recovery for the QA/QC samples will be calculated and used to assess matrix interference. The following will be used when a reference material is used:

$$\%R = 100 * \left(\frac{C_M}{C_{RM}}\right)$$

%*R* = Percent recovery
C_M = Measured concentration of reference material (RM)
C_{RM} = Actual concentration of reference material (RM)

Representativeness

Representativeness will be assured by using a statistically significant number of water samples.

Completeness

A minimum of ninety-five percent (95%) of the water samples collected are expected to yield valid usable data. This will result in the generation of sufficient data to meet the final test design criteria.

$$\%C = 100 * \left(\frac{V}{T}\right)$$

%*C* = Percent completeness
V = Total number of measurements or laboratory results judged valid
T = Total number of measurements or laboratory results

1.6 DOCUMENTATION AND RECORDS

In order to maintain a clear record of sample collection and custody, Regional Board field staff will keep field notes, sample collection records, copies of chain of custody forms, and quality control sample records for each sampling event.

Regional Board staff will maintain Project records in accordance with the QAPP. These records will consist of:

- field logs/notes, quality control logs, and calibration logs

- laboratory analytical reports
- preliminary data reports summarizing field activity and quality control for each sampling event
- miscellaneous correspondence
- final report

The field notes will be entered into bound field log notebooks with pre-numbered pages. Each page of the field logs and field data worksheets will be dated and signed by a member of the sampling team at each sampling station, at the time of sampling, and the following information will be entered into the field log book:

- Observations about the weather and sampling station
- The latitude and longitude of the sampling station, as determined using a global positioning system (GPS) receiver when necessary
- Identification codes (sample I.D.), specific sampling point locations, and sampling methods for all samples taken.
- The instream YSI readings for temperature, dissolved oxygen, pH, conductivity, and Redox Potential**.**
- Sample codes and time and location of preparation for all quality control samples prepared in the field
- Any deviations from QAPP procedures
- Any noteworthy observations
- Flow data

Quality control (QC) samples will be documented in a bound Quality Control Log with pre-numbered pages. The Quality Control Log will document the quality control samples submitted to laboratories and the results of the analysis of these samples. For each QC sample, the quality control log will contain the:

- sample identification code
- supplier of the QC sample
- value reported by the supplier
- date of preparation and submission
- name and signature of the person submitting the QC sample
- laboratory performing the analysis
- analysis method
- reported value from the laboratory

Calibration of the YSI 6600 multiprobe multi-parameter water quality sonde will be documented in a bound calibration log field notebook with pre-numbered pages. The calibration log will contain:

- date and time of calibration
- persons performing the calibration
- signature of one of the persons performing the calibration
- all standard solutions used in calibration, including the source and date of preparation of the standard solution
- initial reading of the YSI when tested against each standard solution, and the temperature of each standard solution at the time of calibration
- any deviations from the QAPP
- any difficulties or relevant notes about the calibration

Upon completion of the laboratory analysis of the samples from each sampling event, the laboratory will prepare and submit to the Project Manager a Laboratory Analytical Summary. The summary should consist of analytical results and chain of custody forms.

A Preliminary Data Report will be developed by the Project Manager, and filed with the Quality Assurance Officer within 10 days from the date the Project Manager receives all lab results for a sampling events. This report will summarize field activities and observations; it also will include field measurements and the results of laboratory analysis. This report also will include a quantitative analysis and discussion of the results of quality control activities, and what these results indicate about the quality of data generated in each sampling event. The report can also include recommendations to improve/modify the QAPP.

The field logs, quality control log, and calibration log along with all additional documentation consisting of any laboratory records and chain of custody forms, will be stored in an organized manner by the Laboratory Director, and will be stored in an accessible manner at the Laboratory.

Once all the sampling is completed, a narrative report will be prepared by the Project Manager for the Quality Assurance Officer and management. At a minimum, this report will discuss any problems encountered and their solutions. Additionally, it will discuss any deviations from this QAPP, if any, as well as the quality of all data.

Quality control records will be maintained documenting the preparation and use of quality control samples and equipment calibration. Chain of custody forms will contain sample identification codes, collection times and locations, and names and signatures of all persons in custody of the samples.

Laboratory records of sample analysis will be collected from each laboratory, showing the samples analyzed, the persons analyzing the samples, the time and date of analysis, and any deviation from standard operating procedures. In addition to maintaining the documentation and records listed above, Regional Board staff will enter all data and meta-data from these forms into a single database, which will be utilized for data validation and data assessment. Meta-data is all the relevant information related to the data itself. The maintenance of the database, as well as the storage of all documentation and records listed above, will be the responsibility of the Project Manager.

1.6.1 TRAINING AND CERTIFICATION REQUIREMENTS

Field samplers must have completed a 40-hour OSHA-approved HAZWOPER training course, and if necessary an 8-hour HAZWOPER yearly refresher course. The Project Manager will ensure that all field samplers have valid and current HAZWOPER training. There are no specialized training/certification requirements needed to perform the Project's activities.

2 DATA GENERATION/DATA ACQUISITION

2.1 SAMPLING PROCESS DESIGN

During the project, Regional Board staff will take samples and collect data from sixty (60) monitoring stations in the Salton Sea at the contributing inflows. The Laboratory will be required to conduct the analyses within the specified holding periods, and in a reasonable time. The Project Manager and QA Officer will evaluate the data generated during each sampling event to determine if any changes in the QAPP are necessary to better meet study objectives. The following paragraphs provide the rationale for the selection of the constituents and monitoring stations.

2.1.1 SAMPLING CONSTITUENTS

The fifteen monitoring stations will be sampled for the constituents listed in Table No. 2, below.

Table 2: Sampling Constituents

Constituent	Units	Method
Orthophosphate	mg/L	USEPA 365.2
Total Phosphorus	mg/L	USEPA 365.2
Ammonia-N	mg/L	USEPA 350.1
Nitrate-N	mg/L	USEPA 300.0
Nitrite-N	mg/L	USEPA 353.2
Total Kjeldahl Nitrogen	mg/L	USEPA 351.3
Total Organic Carbon	mg/L	USEPA 415.1
Hardness (CaCO3)	mg/L	USEPA 130.2
Alkalinity	mg/L	USEPA 310.1
Sulfate	mg/L	USEPA 375.1
Biological Oxygen Demand ($20^{o}C$ BOD_5)	mg/L	USEPA 405.12
Chemical Oxygen Demand	mg/L	USEPA 410.2
Total Suspended Solids	mg/L	USEPA 160.2
Turbidity	NTU	USEPA 180.1
Temperature	^{o}C	YSI Probe
pH	pH Units	YSI Probe
Dissolved Oxygen	mg/L	YSI Probe
Electrical Conductivity (EC)	μmhos/cm	YSI Probe
Chlorophyll A	ug/L	HPLC, Bidigare et al. 2002
Redox Potential	E_h	YSI Probe

The sampling constituents include both causal factor indicators (nutrients that stimulate plant growth) and biological response indicators (assessment of impacts on water quality). The complexity and site-specific

nature of biostimulatory substances require an array of indicators to assess and estimate the load.

Phosphorus
Phosphorus concentration is considered an indicator because algal growth in the Salton Sea may be limited by the availability of that nutrient. It can be measured in several forms. Total phosphorus (TP) and orthophosphates are used largely for setting criteria for lake management. TP (organic and inorganic phosphorus) is important for TMDL load estimations and numeric targets. Orthophosphate is directly available for plant uptake.

Nitrogen
Nitrogen concentration can serve as a valuable indicator in nitrogen limited ecosystems. It can be measured in inorganic (ammonia, nitrate, nitrite) and organic (total nitrogen) forms. Inorganic forms are available for algae uptake. Total Kjeldahl nitrogen is often a good indicator of algal biomass in lakes.

Dissolved Oxygen Concentration
Dissolved Oxygen Concentration is an important indicator where aquatic life is a beneficial user. This parameter is used widely and is established in state water quality standards.

Total Organic Carbon
Total Organic Carbon may indicate the available energy source for the heterotrophic community and their response impact to algal growth. The measurement of total organic carbon also can indicate or be interfered by the amount of suspended sediments.

Total Suspended Solids
TSS has an impact on water transparency and its source may be both algae and sediments. Site-specific quantitative relationships can be developed to predict transparency. TSS reveals the fine suspended solids that frequently are transported with water flow. Phosphorus generally adsorbs to these fine sediment particles. This is one pathway of phosphorus to the Salton Sea.

Electrical Conductivity or Total Dissolved Solids
TDS or EC is a measurement of salinity.

Chlorophyll A
Chlorophyll A is a reliable indicator of algae biomass. This is the photosynthetic pigment of algae cells. Algae are generally either directly (algal blooms) or indirectly (low dissolved oxygen, low pH, high turbidity) responsible for several problems due to excessive nutrient concentration. Both seasonal mean and instantaneous maximum concentrations can be used to determine impairments.

Transparency
Secchi depth is widely used to estimate algal biomass and trophic state, although this estimation can be interfered from a variety of other sources like suspended sediments. Turbidity also is used to estimate both algal biomass and trophic state.

pH
Excess algae levels can be responsible for extreme diurnal fluctuations in water pH. Generally, aquatic organisms are most sensitive to extreme pH levels.

Hardness
Hardness can be represented as the sum of calcium and magnesium concentrations.

Alkalinity
Alkalinity describes the capacity of water to neutralize acid.

Nutrient ratios
Ratios of nutrient concentrations might indicate the relative intensity of algal growth in a calendar season (summer : winter), crop growth season (vegetable crops : perennial crops), response to a specific stream, etc. However, this ratio may be difficult to interpret due to unknown mixing times and unknown algae uptake rates.

Redox Potential
Redox Potential indicates the reducing conditions of the lake/river, dissolved oxygen, and bioavailability of other ions.

Biological Oxygen Demand
Biological Oxygen Demand is a nutrient overenrichment indicator. This parameter reveals the amount of bioavailable carbon (energy) for heterotrophic microorganisms. These organisms are active and important in nitrogen and phosphorus cycles. Therefore, this parameter may indicate microbial activity and nutrients available for algae uptake.

Chemical Oxygen Demand
Chemical Oxygen Demand is used to measure everything that can be oxidized in the water sample (organic and inorganic).

2.1.2 MONITORING STATIONS

Regional Board personnel conducted field inspections in the area of the lake to ascertain general characteristics (e.g., direction of flow, cross-sectional areas, flow) of tributaries, and to identify potential sampling points. Currently, almost all drains and rivers will be monitored. However, future monitoring stations will be chosen based on best professional judgment, locations of contributing streams, previous sampling results, direction of flow in the lake, inflows, and site accessibility. Visual inspections on flow direction and flow rate of the small drains will be conducted prior to sampling to indicate any backflow from the Salton Sea to the drains. Table No. 3 shows the monitoring stations.

Table 3: Description of Sampling Stations

Site No.	Site Label	Description
01	FD	F Channel, Riverside County
02	ED	E Channel, Riverside County
03	OG	Oasis-Grant, Riverside County
04	DD	D Channel, Riverside County
05	CD	C Channel, Riverside County
06	AV83	Avenue 83 Drain, Riverside County
07	AV79	Avenue 79 Drain, Riverside County
08	LO	Lincoln-Oasis Drain, Riverside County
09	AC	A Channel, Riverside County
10	AV76	Avenue 76 Drain, Riverside County
11	AV74	Avenue 74 Drain, Riverside County
12	CVSWC	Coachella Valley Storm Water Channel, Riverside Co.
13	JST	Johnson Street Drain, Riverside County
14	GRST1	Grant Street Drain, Riverside County
15	GRST2	Grant Street 0.5 Drain, Riverside County
16	HST1	Hayes Street Drain, Riverside County
17	HST2	Hayes Street 0.5 Drain, Riverside County
18	GAST1	Garfield Street Drain, Riverside County
19	GAST2	Garfield Street 0.5 Drain, Riverside County
20	AST1	Arthur Street Drain, Riverside County
21	AST2	Arthur Street 0.5 Drain, Riverside County
22	CSTE	Cleveland Street East Drain, Riverside County
23	CSTW	Cleveland Street West Drain, Riverside County
24	CAC	Caleb Channel, Riverside County

25	CST2	Cleveland Street 0.5 Drain, Riverside County
26	MST	McKinley Street Drain, Riverside County
27	SCR	Salt Creek, Riverside County
28	ND5	Niland 5 Drain, Imperial County
29	ND4	Niland 4 Drain, Imperial County
30	ND3	Niland 3 Drain, Imperial County
31	ND2	Niland 2 Drain, Imperial County
32	ND1	Niland 1 Drain, Imperial County
33	ZD	Z Drain, Imperial County
34	WD	W Drain, Imperial County
35	UD	U Drain, Imperial County
36	TD	T Drain, Imperial County
37	SD	S Drain, Imperial County
38	RD	R Drain, Imperial County
39	QD	Q Drain, Imperial County
40	PD	P Drain, Imperial County
41	OD	O Drain, Imperial County
42	ARO	Alamo River Outlet (Garst Road), Imperial County
43	VD3	Vail 3 Drain, Imperial County
44	PUMD	Pumice Drain, Imperial County
45	VD5	Vail 5 Drain, Imperial County
46	VD5A	Vail 5A Drain, Imperial County
47	VD6	Vail 6 Drain, Imperial County
48	VCD	Vail Cut-Off Drain, Imperial County
49	NRO	New River Outlet, Imperial County
50	TRD12	Trifolium 12 Drain, Imperial County

51	TRD13	Trifolium 13 Drain, Imperial County
52	TRD14A	Trifolium 14A Drain, Imperial County
53	TD1	Trifolium 1 Drain, Imperial County
54	TRSD	Trifolium Storm Drain, Imperial County
55	TRD18	Trifolium 18 Drain, Imperial County
56	POED	Poe Drain, Imperial County
57	TRD19	Trifolium 19 Drain, Imperial County
58	TRD20	Trifolium 20 Drain, Imperial County
59	TRD22	Trifolium 22 Drain, Imperial County
60	TRD23	Trifolium 23 Drain, Imperial County

To help determine the spatial distribution in the area of the monitoring station, the monitoring station consists of three (3) sampling points (S1, S2, and S3), distributed along the surface and perpendicular to the flow of the canal/drain being monitored. At the outlets of the New and Alamo Rivers, the sampling points are to be spaced at approximately equal intervals from each other and from the edge of the canal/drain (i.e., at a distance equal to w/4, where "w" is the top width of the cross-sectional area). Figure No. 1, below, illustrates this.

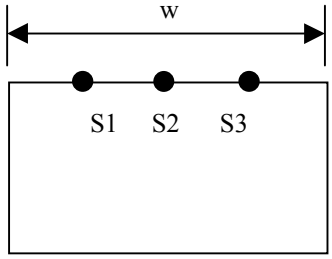

Figure 1: Sampling Points at Monitoring Stations

However, at the other monitoring locations, only one point will be used because of the narrowness of the drains.

2.2 SAMPLING METHODS REQUIREMENTS

In order to obtain comparable and accurate results, appropriate sampling protocols must be followed uniformly at each sampling station for each constituent during all sampling events. The following two sections describe sampling and handling procedures for each sample parameter.

2.2.1 BIOLOGICAL, CHEMICAL, AND PHYSICAL INDICATORS

To prevent sample contamination, one pre-cleaned sample bottle will be dedicated for each sample parameter or parameters at each sampling point. Grab samples will be taken at one (1) foot below water surface (bws) at each sampling point of each monitoring station using a 1000-ml polyethylene pre-cleaned bottle attached to the end of a "Swing Sampler®". Then, with the sampler downstream of the bottle, the bottle will be plunged downward approximately 1 foot into the water, and allowed to fill with the opening pointed slightly upward into the current. The bottle then will be raised out of the water, and the 1000-ml sample will be distributed immediately to the appropriate, uniquely-labeled sample bottles (470-mL). The bottles then will be immediately capped tightly and placed into ice chests. The bottles will be obtained from the laboratory contractor and will contain the required preservatives.

In order to ensure accurate results, acceptance requirements for all sample containers are as follows:

- Inorganic Sample Storage Containers are to be certified clean and pre-preserved
- Organic Sample Storage Containers are to be certified clean and pre-preserved
- The laboratory contractor must submit written documentation verifying sample container specifications

Table 4 shows required containers, preservatives, techniques, and holding times for all constituents.

Table 4: Required Containers, Preservatives, Techniques, and Holding Times

Constituent	Container	Preservation Technique	Holding Time
Orthophosphate	1-L low density polyethylene bottle with poly-lined, white poly cap	Cool below 4 °C	28 Days
Nitrite			
Nitrate			
Total Kjeldahl Nitrogen			
Total Suspended Solids			7 days
Turbidity			48 hours
Biological Oxygen Demand			48 hours
Chemical Oxygen Demand			
Sulfate			28 days
Alkalinity			
Total Phosphorus	1-L low density polyethylene bottle with poly-lined, white poly cap	Cool below 4 °C; Sulfuric Acid Preservative (pH<2)	28 days
Ammonia			
Total Organic Carbon	VOA vial	Cool below 4 °C	28 days
Chlorophyll A	1-L low density polyethylene bottle with poly-lined, white poly cap	Cool below 4 °C; Mg CO3	Analysis should be performed ASAP following sampling
Hardness (CaCO3)	1-L low density polyethylene bottle with poly-lined, white poly cap	Cool below 4 °C; Sulfuric Acid Preservative (pH<2)	6 months

2.2.2 FIELD MEASURED PARAMETERS

A YSI 6600 Multiprobe will be used to measure the levels of dissolved oxygen (DO), pH, temperature, electrical conductivity (EC), and redox potential at each sampling point. The probe will be deployed at one (1) feet bws. The readings from the YSI 6600 probe will be taken within, at most, a two-foot radius of the point of sample collection, simultaneously as the samples for lab analyses are collected. The sample ID numbers, YSI 6600 readings, field observations, and any deviation from standard operating procedures will be recorded in the field notebook immediately following collection of each sample. Also, stream flow will be obtained from USGS, IID, and CVWD measurements.

2.3 SAMPLE HANDLING AND CUSTODY REQUIREMENTS

Each sample container will be labeled with a unique sample identification code, as well as the date and location where the sample was taken. The sample ID code is of the format:

Project - Sampling Station – Location - Sample Type – Sample Parameter

The location refers to the cross-section, which is numbered from left to right when facing downstream. Sample type indicates a sample (0), duplicate (1), spike (2), MS/MSD (matrix spike/matrix spike duplicate) (3/4). Nitrate, nitrite, ammonia, total Kejldahl nitrogen, orthophosphates, total phosphorus, total organic carbon, calcium carbonate, sulfate, biological Oxygen demand, chemical oxygen demand, chlorophyll A, Turbidity, and total suspended solids parameters are indicated by NO3, NO2, NH3, TKN, o-PO4, Total PO3, TOC, CaCO3, SO4, BOD, COD, CHL A, TUR, and TSS respectively. Waterproof ink will be used to encode the self-adhesive sample labels. The labels will be affixed to the sample bottles according to manufacturer's specifications.

All samples for lab analyses will be placed in waterproof plastic "zip lock" bags and immediately be stored in an ice chest. Samples from each cross-section shall be stored in separate zip lock bags. The ice chest will contain sufficient ice to maintain the samples at a temperature below 4°C at all times until they are relinquished to the appropriate laboratory personnel. The samples will be delivered to the appropriate laboratory, taking into consideration the holding times listed in Table 4. A ten-day notice will be given to the analytical laboratory prior to the delivery of samples. Samples will be retained in the custody of Regional Board staff until they are delivered to laboratory personnel.

All samples will be delivered with chain of custody forms. A sample chain of custody form is included in Appendix II. Any violation of holding times or other sample handling and custody requirements will be reported to the Project Manager and the QA Officer, and recorded in the quality control records, and taken into consideration during data validation, as described in section 4.1.

2.4 ANALYTICAL METHODS REQUIREMENTS

The laboratory will analyze all samples except the field measurements. Spike samples for laboratory analyses will be obtained from Environmental Research Associates, Arvada, CO. All samples will be analyzed using USEPA approved methods. The process for selection of laboratories for this sampling event involved reviewing Standard Operating Procedures (SOPs) (Appendix III and Attachment B), QA documents, corrective action plans, detection limits, and laboratory location.

2.5 QUALITY CONTROL REQUIREMENTS

In order to assess whether data quality requirements are being met, a number of quality control checks will be implemented, as described below:

- Duplicate or co-located samples will be taken for all constituents at approximately 10% of the sampling points.

- Field blanks for inorganic parameters will be submitted to the current laboratory contractor at a rate of 1 blank/day/event.

- Spike samples, containing a known concentration of a specific chemical, will be obtained from Environmental Resource Associates and submitted to the current laboratory contractor along with the other samples. The 5-mL samples will be diluted with 1 liter of water to a known concentration. Two spike samples for every chemical parameter will be submitted every three sampling events. In addition, a dilution water blank will submitted for analysis with the spike samples to evaluate any bias. All laboratory results must be within 20% of the concentration value submitted by Environmental Research Associates.

- Matrix effects for inorganics will be evaluated by the collection of two double volume samples at two separate locations. These two samples will be submitted to the current laboratory contractor with the designation "QA/QC" samples. These known samples are called matrix spike (MS) and matrix spike duplicates (MSD). The current laboratory contractor will analyze, spike, and reanalyze the samples, and will calculate a percent recovery. This value will be used to ascertain any matrix effects.

- Temperature blanks will be included in each ice chest submitted to a lab. The temperature of these blanks will be analyzed using chain of custody to ensure that the samples have been maintained at the prescribed temperature (4^{o}C).

All QC samples will be stored and labeled following the same methods. QC samples will be submitted to the labs as blind samples. Table No. 5, below, summarizes the QC samples to be utilized.

Table 5: Quality Control Sample Requirements

Quality Control Samples	Approximate Number Of Samples/Event
Duplicate Samples (10%/Event, 6 for each parameter or group of parameters)	60
Field Blanks (1/day/event)	4
Spike Samples (2 for each appropriate parameter per three sampling events) Dilution Water Blank	14 1
Matrix Spike Samples (2 double volume samples at two separate locations per sampling event)	4

2.6 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE REQUIREMENTS

Proper maintenance procedures will be followed and documented. The YSI 6600 Multiprobe will be tested, inspected, and serviced as necessary prior to each sampling event, pursuant to procedures recommended in the YSI, Inc., *6-Series Environmental Monitoring Systems Operations Manual*. Its batteries will be checked at the beginning of the first sampling event and replaced as appropriate. The EC and pH probes will be tested using a 1,000 μmhos/cm EC solution and a pH solution (4, 7, 10) respectively, prepared by the Regional Board laboratory. The DO probe will be tested using saturated air. All probes will be visually inspected for damage at each sampling point prior to field measurements, and will be serviced as appropriate.

2.7 INSTRUMENT CALIBRATION AND FREQUENCY

The YSI 6600 will be calibrated prior to the beginning of each day's sampling pursuant to the calibration procedures recommended in the YSI, Inc., *6-Series Environmental Monitoring Systems Operations Manual* (1999). For subsequent sampling events, the YSI 6600 will be calibrated at the lab following the Manual prior to the beginning of sampling events. Results of calibration measurements will be documented in the field log notebook and presented to the QA Officer. The DO probe will be calibrated using tap water. A three-point calibration, using pH 4, pH 5 and pH 10 calibration standards, will be performed on the pH probe. Table 6, below shows the parameter specifications for the YSI 6600.

Table 6: Parameter Specifications for the YSI 6600

Parameter	Operating Range	Accuracy	Resolution	Calibration Standard
pH	0 to 14 units	± 0.2 units	0.01 units	3-pt, with pH buffered solutions (pH 4, 7 & 10)
Temperature	– 5 to 45 °C	± 0.15 °C	0.01 °C	* not required
Dissolved Oxygen	0 to 50 mg/L	0-20 mg/L, ± .2 mg/L 20-50 mg/L, ± 0.6	0.01 mg/L	% air saturation
Conductivity	0 to 100 mS/cm	± 0.5% of reading + 0.001 mS/cm	0.001 mS/cm	KCl

*As per the manufacturer's specifications. Temperature accuracy is verified every 6 months using a thermometer which is calibrated with a thermometer traceable to the National Institute of Standards and Technology.

2.8 INSPECTION/ACCEPTANCE REQUIREMENTS FOR SUPPLIES/CONSUMABLES

All supplies and consumables will be documented and inspected upon receipt and before sampling. Seals need to be intact. Sampling bottles should be clean and contain the proper preservatives. A log on the inspection/acceptance process will be kept. Records will include identification number, item description, date received, date accepted, expiration date, handling and storage conditions, and name of the inspector.

2.9 DATA ACQUISITION REQUIREMENTS (NON-DIRECT METHODS)

Several other institutions have analyzed the Salton Sea for many constituents. Previous data relative to this project will be used after checking its quality. Criteria for accepting the already-collected data include its representativeness of similar conditions, any documented bias, logical methods of evaluating the data and its applicability to this project, and data summarization. The QAPP Developer will supply previous data to the QA Officer as requested.

2.10 DATA MANAGEMENT

2.10.1 DATA STATISTICAL ANALYSIS

Data from the sampling methods will be analyzed statistically using the Spreadsheet Excel software. Data will be entered into Excel in columns, with one column for each method. Descriptive Statistics (e.g. mean, standard deviation, and coefficient of variation) will be computed for each column.

The mean is calculated as the sum of all observations divided by the total number of observations. The standard deviation is a measure of the spread of the data, and can be calculated as the square root of the sample variance. The variance measures the variability or spread of the observations about the sample mean and can be calculated as the sum of the squared differences from the sample mean divided by the number of observations less one. Coefficient of variation is calculated as the standard deviation divided by the mean. A coefficient of variation of more than one (1.0) will indicate that the data are not normally distributed.

3 ASSESSMENT AND OVERSIGHT

3.1 ASSESSMENT AND RESPONSE ACTIONS

Surveillance of the records and overall status of the project will be conducted by the QA Officer to ensure that all requirements of the QAPP are met. Surveillance will be conducted after each sampling event, after all laboratory results have been received for that sampling event.

A Technical Systems Audit also will be performed by the QA Officer. During this audit, the QA Officer will examine field activities and record-keeping procedures to assess conformance to the QAPP. This audit will take place any time, and at the discretion of the QA Officer. Any non-conformance with the QAPP will be corrected and documented as described in Section 4. Performance Evaluations of laboratories will be conducted through the use of quality control samples, namely split samples and matrix spike samples. A review of the laboratory's QA for this project also will be conducted.

At the completion of the project, but prior to producing the final report, an Audit of Data Quality will be performed to assess the handling of all data and to correct any errors found in the project database. A Data Quality Assessment also will be performed in which statistical tools will be used to determine whether the data met all assumptions that the Data Quality Objectives and data collection design were developed under, and if the total error in the data is tolerable. The total error present will be quantified to determine if the quality of the data is adequate to support a determination regarding the influence of contributing inflows on the water quality of the Salton Sea.

3.2 REPORTS TO MANAGEMENT

Upon completion of the project, the Project Manager will prepare a final Project report. This final report will include a summary of the activities performed, the resulting data, and the quality of the resulting data, and will identify any samples that indicate violations of Water Quality Standards. This final report will contain an assessment of whether or not contributing streams in the Salton Sea were polluting the lake during the time period of the study, and a statement of the confidence with which the assessment was made, based on the quality of the data. This report will be forwarded to management, as well as appropriate officials from Imperial County, Imperial Irrigation District, Coachella Valley Water District, Salton Sea Nutrients TMDL TAC Members, and Riverside County.

4 DATA VALIDATION AND USABILITY

4.1 DATA REVIEW, VERIFICATION, VALIDATION, AND RECONCILIATION

4.1.1 DATA REVIEW

Regional Board staff will be responsible for validating the project's data to ensure that QA guidelines have been followed. QA performed by the Regional Board will ensure that the data transfer process is error-free, that results reported are reasonable in relation to the distribution of previously reported results by Imperial County and the Regional Board, and that samples were analyzed in accordance with procedures in Table No. 2 and 4.

After each sampling event, the Project Manager will review the field notes and field data generated to assess adherence to the project sampling design in terms of the spatial distribution of sampling locations. Departures from the sampling design will be considered in the design of each subsequent phase of sampling. Deviations from the sampling design may change the data needed to characterize the system. Departures from the sampling design also may be due to unforeseen field conditions, which may require adjustment of the sampling design. Significant departures from the project sampling design and responses to those departures will be noted in the project database, as well as the Audit of Data Quality, and the final report. In the Data Quality Assessment, the Project Quality Assurance Manager and Project Manager will consider the effects of any departures from the sampling design on the overall completeness of the data generated, and thus the usability of the data set for drawing conclusions.

4.1.2 DATA VERIFICATION

Verification of adherence to the sample collection and equipment decontamination procedures contained in Attachment A of this report will be determined through the field records, Technical Systems Audit, and project surveillance identified above. All information will be considered in the final Audit of Data Quality. Some departures from the sample collection procedures are unacceptable, and will result in data that will not be considered valid for use in this study. Unacceptable departures from sample collection procedures include the use of contaminated sampling bottles, lack of critical sample collection information, or any other activity which would result in cross-contamination or incorrect identification of samples.

Departures from the sample handling and custody procedures contained in section 2.3 will be determined through the review of chain of custody forms and laboratory analysis forms. In order for data to be considered valid for meeting the data quality objectives of this study, all samples' chain of custody forms must be in the possession of the project manager, and strict adherence to holding times and temperatures must be followed. Data generated from samples that do not meet these requirements will not be considered valid for use in this study.

Verification of proper calibration of the YSI 6600 will be performed during the audit of data quality through a review of the quality control records. Calibration values also will be assessed to determine the potential error in field measurements. Measurements will not be made unless the instrument is properly calibrated.

4.1.3 DATA VALIDATION

Validation of laboratory data will be performed in the Audit of Data Quality by assessing the results of QC

sample analyses. Inorganic lab data will be validated for precision, accuracy, and completeness according to criteria in Table No. 1.

Data for inorganic QC samples falling outside the specified precision will be re-analyzed. The laboratory will be notified of this procedure. Should the analyses confirm the previous results, the sample collection and sample handling procedures will be labeled as "suspect" and, subsequently, re-evaluated. Any value that cannot be confirmed, based on the acceptable recovery for a split sample, will be rejected.

Lab data results for all other samples also will be range-checked for outliers by comparing lab results with Regional Board Trend Monitoring Program data. Values falling outside the expected ranges will be labeled as "suspect" and further investigated. Values, which are expected to be normally distributed, but labeled "suspect", will be further evaluated and rejected using Chauvenet's Criterion (i.e., if the value deviates from the mean value of the data set by more than 1.96$\forall$, where $\forall$ is the standard deviation for the data set). Results that clearly depart from the established distribution will be identified, and Regional Board staff will discuss these results with data providers to ensure accuracy.

The data then will be entered into a database by Regional Board staff. It is conceivable that errors could occur in entering the data (e.g., transposing the decimal point for a particular result or keying in the wrong Sample ID). Therefore, once a data set has been entered into the database, all records will be checked by the Project Manager to ensure accuracy.

Regional Board staff will discuss missing data with the laboratories submitting the data. In some cases, missing data will be denoted as missing in reports. For all missing data, and any other data requiring special explanation, qualifiers will be included in the database and in data reports. Missing data will be designated as "NR," meaning *Not Reported*.

The Regional Board Quality Assurance Manager will be responsible for validation and final approval of all data for use in this study. The final project report will contain a discussion of relevant information obtained through the Audit of Data Quality about the quality, validity, completeness, and limitations of the data obtained in this study.

Data objectives for this project do not require a full, formal, and independent data validation. The data has no legal requirement for independent validation. Although the data is considered legally defensible as presented herein, all records will be available for independent evaluation should the need arise at a later date.

The current laboratory contractor will communicate with the Quality Assurance Officer about any problem and need for data reconciliation.

5 HEALTH AND SAFETY PLAN

5.1 CONTAMINATION CONTAINMENT ZONES

Upon arrival at a particular sampling station, an exclusion, decontamination, and support (clean) zone will be established and maintained at the sampling station throughout the duration of sampling at the particular station. The process of establishing and breaking down containment zones will be repeated at each sampling station. The exclusion zone consists of the shore of the lake and extends ten (10) feet inland. The decontamination zone will be set up adjacent to the exclusion zone, extending 10 feet inland of the exclusion zone boundary. The decontamination zone will be used for personnel and equipment decontamination and will include wash water, soap, paper towels, and trash bags. All contaminated solid waste material will be placed in trash bags for proper disposal. Only biodegradable antibacterial soap will be used at the site. Wash water runoff will be contained and disposed of properly. The clean area will be set inland of the decontamination zone.

5.2 PERSONAL PROTECTIVE EQUIPMENT

The general concerns at sampling sites are the potential exposure to pathogens and toxicants present in waters being sampled, the risk of being struck by an automobile when taking samples near the roadside or off of bridges, and the risks of sunburn, excessive heat exposure, and insect and possibly snake bites. In addition, the sampling crew should be aware of the risk of falling into a drain. No less than three experienced samplers will be out in the field at one time. (The sampling crew also will have a functional cellular phone in one of the vehicles).

- Any member of the sampling team has the authority to stop the sampling event when he/she determines that conditions at the site (e.g., rain, dust, local emergency, etc.) preclude safe sampling. A Hazard Evaluation Plan (HEP) will be done for each day of sampling

- The following precautions will be taken to reduce the risk of being around automobile traffic. At roads, bridge crossings, and wherever traffic reasonably is expected to be present, traffic cones will be set at approximately 30-foot intervals to form at least a 5-foot wide “safety corridor” between the traffic and sampling crew. At the beginning and end of the corridor, one State vehicle must be parked as part of the “safety corridor”. The parked vehicle and traffic cones must be clearly visible to on-coming traffic from a distance of at least 120 feet. Samplers also will be required to wear orange vests.

- To reduce the risk of heat exposure and sunburn, samplers will wear sunscreen and the vehicle will always have plenty of cold drinking water supplied by the Project Manager. If any of the samplers begin to experience symptoms of heat exhaustion, such as cramps or dizziness, he or she will immediately be removed from the sun and given plenty of cool liquids. If these symptoms persist, he or she will be taken to the nearest hospital.

- Extra caution should be used when working near or around drains to reduce the risk of potentially falling in.

- To reduce the risk of insect bites, samplers will use insect repellent.

- To reduce the risk of snake bites, samplers will check for snakes prior to entering the area. If a snake bite occurs, ice will be placed on the bite. The sampler will be transported immediately to the nearest medical facility.

- The main health threat during sampling is exposure to pathogens and toxicants through incidental and accidental contact with Salton Sea water. The following personal protective equipment will be used for those directly handling samples at the Salton Sea:

    - Face Shield
    - Latex Examination Gloves (inner gloves)
    - Nitrile Gloves (outer gloves)
    - Tyvek Suit or isolation gown
    - Boot covers

5.3 PERSONNEL DECONTAMINATION PROCEDURES

The Support Zone must not be entered with contaminated PPE (Personal Protective Equipment). All team members coming out of the Contaminated Zone must proceed immediately to the Decontamination Zone and use the following decontamination procedures before proceeding to the Clean Zone:

1. Remove boot covers and place them in a plastic bag;

2. Wash outer rubber gloves with antibacterial soap prior to removal of any other PPE. Place outer gloves in the storage bin labeled "Decontamination PPE No. 1";

3. Carefully remove Tyvek suit and place it in the storage bin labeled "Decontaminated PPE No. 2" (making sure not to let skin contact the outside of the suit);

4. Remove face shield and place it in a plastic bag;

5. Remove latex gloves carefully to avoid contact with bare skin and dispose of them in the trash bag. Thoroughly wash hands with antibacterial soap; and

6. Properly dispose of wash water.

Note: everything that is touched (pens, pencils, rinse water bottles, probes, etc.) with dirty gloves could be contaminated. Avoid touching these items with bare skin.

5.3.1 EMERGENCY NUMBERS AND FACILITIES

Sampling personnel should call 911 in the event of an emergency. The hospital nearest the sampling location can be:

Name: Kennedy F. Memorial Hospital
Address: 47111 Monroe Av., Indio, CA
Phone: (760) 347-6191

Name: Pioneers Memorial Hospital
Address: 207 W. Legion Rd., Brawley, CA
Phone: (760) 347-6191

Name: El Centro Regional Medical Center
Address: 1415 Ross Av., El Centro, CA

Phone: (760) 339-7100

Other emergency numbers include:

Name: Imperial County Sheriff – Dispatch
Address: 328 Applestill Road
P.O. Box 1040
El Centro, CA 92244
Phone: (760) 339-6311

Name: Riverside County Sheriff – Dispatch
Phone: 911 (emergency calls only)
1-800-950-2444 (emergency and crime reporting dial)

In case of an emergency, sampling personnel also should contact the QA as soon as practical at (800) 796-7363, PIN 102-9073.

5.3.2 AFTER SAMPLING

Place samples into an ice chest filled with wet ice, and keep water drained from ice chests to avoid soaking container labels. Due to relatively short holding times, samples are to be delivered expeditiously to the current laboratory contractor. Contaminated equipment should be packed in designated containers for transport to the Regional Board office. Decontaminate and properly clean ALL items that were exposed in the field. Make copies of field notes and put originals in the appropriate binder.

5.4 DECONTAMINATION PROCEDURES

Please see Attachment A.

6 BIBLIOGRAPHY

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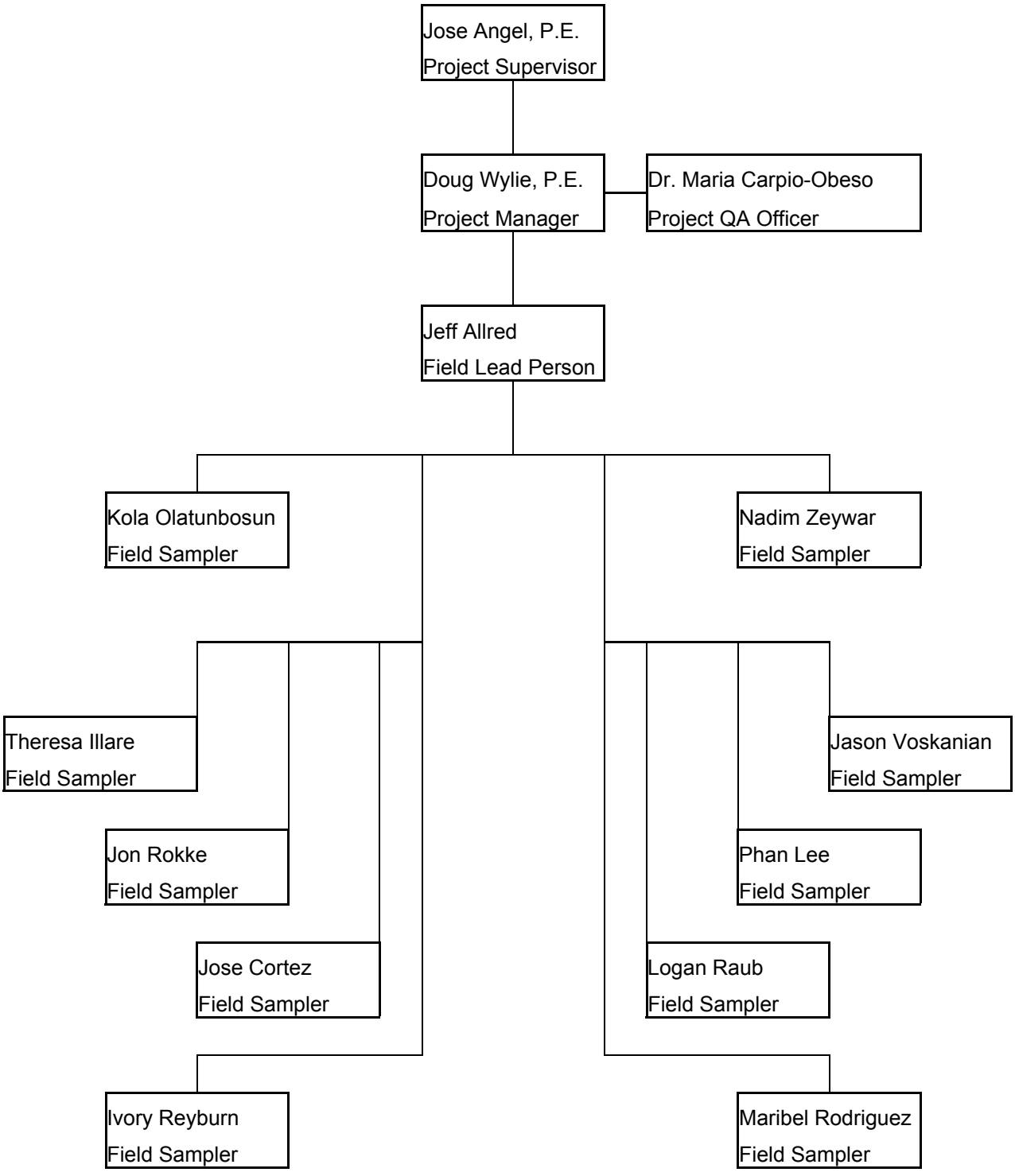
7 APPENDIX

APPENDIX I, PROJECT ORGANIZATION CHART



APPENDIX II: SAMPLE FORMS

CHAIN OF CUSTODY RECORD

E.S. BABCOCK & SONS, INC.

6100 Quail Valley Court
Riverside, CA 92507
(909) 653-3351
FAX (909) 653-1662

Lab #: ______ Invoice No. ______

Project No.	Project Name / Location							
Samplers: (signature)								
Description	Sampled Date	Sampled Time	Determination Requested	Number of Containers	Condition of Sample: Sealed	Condition of Sample: Chilled	Condition of Sample: Preserved	Remarks

Relinquished By:	Date/Time	Received By:	Relinquished By:	Date/Time	Received By:
Relinquished By:	Date/Time	Received By:	Received For Lab By:		Date / Time

Effective Date: 08/25/00 6:28 PM
Revision #4.0
Page: 1

I19

METHOD #: EPA 300.0, and 9056
SM 4110 B
CA DHS IC Rev 0

TITLE: The Determination of Inorganic Anions in Water by Ion Chromatography

ANALYTE:	CAS #
Chloride Cl	7782-50-5
Fluoride F	7782-41-4
Nitrate (NO_3)	
Nitrite (NO_2)	
Phosphate (PO_4)	
Sulfate (SO_4)	
Perchlorate (ClO_4)	
Para-Chlorobenzene Sulfonic Acid (PCBSA)	

INSTRUMENTATION:

IC: Dionex 500DX and 120DX (see sec. 6.2)
Data Handling: Pentium Processor with Peak-Net software on Windows NT platform.
Printer: HP Laser Jet 2100
Autosampler: Alcott Micromeritics 728

1.0 Scope and Application

1.1. This method covers the determination of the following inorganic anions.

		RL, mg/L
1.1.1. Method A.		
1.1.1.1.	Fluoride	0.1
1.1.1.2.	Chloride	1
1.1.1.3.	Nitrate-N	0.2
1.1.1.4.	Nitrite-N	0.1
1.1.1.5.	Phosphate-P	0.05
1.1.1.6.	Sulfate	0.5
1.1.1.7.	PCBSA	10
1.1.2. Method C		
1.1.2.1.	Perchlorate	0.004

Note: RL = Reporting Limit

1.2. The matrices applicable to each method are shown below:
1.2.1. Drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids (after extraction 2.3),
1.2.2. Drinking water and reagent waters.

1.2.3. Drinking water, groundwater and reagent waters.

1.3. The Single Laboratory Method Detection Limit (MDL, defined in section 13.1) for the above analytes is listed in Tables 1A through 1C. The MDL for a specific matrix may differ from those listed, depending upon the nature of the sample.

1.4. The working range for these analytes is as follows:

1.4.1.	Fluoride	0.1-5 mg/L
1.4.2.	Chloride	1-250 mg/L
1.4.3.	Nitrate-N	1-250 mg/L
1.4.4.	Nitrite-N	0.1-5.0 mg/L
1.4.5.	Phosphate-P	0.05 -5.0 mg/L
1.4.6.	Sulfate	1-400 mg/L
1.4.7.	Perchlorate	0.004-0.25 mg/L
1.4.8.	PCBSA	1-500 mg/L

1.5. This method is recommended for use only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatogram. Each analyst must demonstrate the ability to generate acceptable results with this method, using the procedure described in Section 10.2.

1.6. When this method is used to analyze unfamiliar samples for any of the above anions, anion identification should be supported by the use of fortified sample matrix covering the anions of interest. The fortification procedure is described in Section 11.9.

2. Summary of Method

2.1. An aliquot Sample (25 µL for Method A, and 740 µL for Method C)of sample is injected into an eluent stream and passed through a series of ion exchangers. The system is comprised of a guard column, separator column, and suppressor device. These separate the ions based on their affinity for a low capacity, strongly basic ion exchanger. They are then directed onto a strongly acidic cation exchanger where they are converted to their highly conductive acidic forms. The conductivity of these acid forms is measured. Identification is based on retention time. Quantitation is based on peak height or peak area.

2.2. The main differences between Method A and C are the separator columns, guard columns and eluents. Sections 6 and 7 will elicit the differences.

2.3. In order to use this method for solids an extraction procedure must be performed (See Sec 11.10).

3. Definitions (see SOP Q15 for further definitions)

3.1. Stock standard solution - a concentrated solution containing a single certified standard that is a method analyte. Stock standard solutions are used to prepare calibration standards.

3.2. Calibration standards (CAL) - a solution of analytes prepared in the laboratory from stock standard solutions and diluted as needed and used to calibrate the instrument response with respect to analytic concentration.

3.3. Quality control sample (QCS) - a solution containing known concentrations of analytes, received quarterly from an outside vender (such as ERA). The analyzing laboratory uses this solution to demonstrate that it can obtain acceptable identifications and measurements with a method.

3.4. Performance evaluation sample (PE) - a solution of method analytes acquired from an outside source. A volume of the solution is added to a known volume of reagent water and analyzed with procedures used for samples. Analyte true values are unknown to the analyst.

3.5. Initial Calibration Check ICC (or Calibration Check standard) - a solution of analytes prepared in the laboratory by adding appropriate volumes of the stock standard solutions to reagent water used to evaluate the performance of the instrument system right after a calibration is performed. The low-level calibration standard is reinjected as well as the LCS to satisfy this requirement.

3.6. Laboratory duplicates (DUP) - two aliquots of the same sample that are treated exactly the same throughout laboratory analytical procedures. Analyses of laboratory duplicates indicate precision associated with laboratory procedures but not the sample collection, preservation, or storage procedures.

3.7. Laboratory fortified sample matrix (LFM) or Matrix Spike (MS) - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM (or MS) is analyzed

exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM (or MS) corrected for background concentrations.

3.8. Laboratory Control Sample (LCS) referenced in the method for oxyhalides as the Continuing Calibration Check and in the method for perchlorates as the Laboratory Fortified Blank and Instrument Performance Check. An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control.

3.9. Reporting Level Check A standard is run daily at the reporting limit to demonstrate that the laboratory is capable of making accurate and precise measurements at the required reporting detection limit (a). Once a year this standard is run seven times in a row as part of a detection limit study (b).

3.10. Method Blank (MB) An aliquot of D.I. water is analyzed at the beginning of a run and every ten samples.

4. Interferences

4.1. Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or spiking can be used to solve most interference problems.

4.2. The water dip or negative peak that elutes near and can interfere with the fluoride peak can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent (7.3 100X) to 100 mL of each standard and sample.

4.3. Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

4.4. Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems. Caution: filtration may remove perchlorate.

4.5. Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L this interference may not be significant, however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

4.6. The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

4.7. The quantitation of unretained peaks should be avoided, such as low molecular weight organic acids (formate, acetate, propionate, etc.) which are conductive and coelute with or near fluoride and would bias the fluoride quantitation in some drinking and most waste waters.

5. Safety

5.1. Normal, accepted laboratory safety practices should be followed during reagent preparation and instrument operation. No known carcinogenic materials are used in this method.

5.2. See SOP S01 , Concentrated Acids and Bases
SOP S02 – Compressed Gas Cylinder Handling
SOP S03 – Spill Control Policy

6. Apparatus and Materials

6.1. Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2. Ion chromatograph - Analytical system complete with ion chromatograph and all required accessories including syringes, analytical columns, compressed gasses and detectors.

6.2.1. Anion guard column: A protector of the separator column. If omitted from the system the retention limes will be shorter. Usually packed with a substrate the same as that in the separator column.

6.2.2. Anion separator column:
6.2.2.1. Anion separator column (Method A):

6.2.2.1.1. AS-4A 4mm Dionex Column
6.2.2.1.2. AG4A 4mm Dionex Guard Column
6.2.2.2. Anion separator column (Method C):
6.2.2.2.1. AS-5 Dionex Column
6.2.2.2.2. AG-5 Dionex Guard Column
6.2.3. Anion suppressor column:
6.2.3.1. Anion suppressor column (Method A): Anion self-regenerating ASRS-11.
6.2.3.2. Anion suppressor column (Method C): Anion micromembrane suppressor AMMS-11
6.2.4. Detector – CD20 conductivity cell.

7. Reagents and Consumable Materials

7.1. Sample bottles: Glass or polyethylene of sufficient volume to allow replicate analyses of anions of interest.

7.2. Reagent water: Nanopure, free of the anions of interest. Water should contain particles no larger than 0.20 microns with a conductance of <0.1uS/cm.

7.3. Eluent solution:
7.3.1. Method A: Dissolve 0.571 g sodium bicarbonate ($NaHCO^3$) and 0.763 g of sodium carbonate (Na^2CO^3) in 1 liter of nanopure water (7.2) and dilute to 4 liters.
7.3.2. Method C: Add 19.2 mL of 50% NaOH and 0.4765 g of 4-cyanophenol to 1 liter of nanopure water (degassed by Nanopure process DHS-IC-Rev 0 7.2). Dilute to 2 liters.

7.4. Regeneration solution (MicroMembrane Suppressor) Concentrated Sulfuric Acid:
7.4.1 Method C: 3.9 mL per 4 liters nanopure water.

7.5. Stock standard solutions, 1000 mg/L (1 mg/mL): Stock standard solutions are purchased as certified solutions.

Note: Stability of standards: Stock standards (7.5) are stable for at least one month when stored at 4-C. The bottle expiration dates are used as a guideline. Dilute working standards should be prepared each time a calibration is performed. LCS solutions are prepared weekly except those that contain phosphate which are prepared fresh daily (c).

8. Sample Collection, Preservation and Storage

8.1. Samples should be collected in scrupulously clean glass or polyethylene bottles.

8.2. Sample preservation and holding times for the anions that can be determined by this method are as follows.

Analyte	Preservation	Holding Time
Chloride	None required	28 days
Fluoride	None required	28 days
Nitrate-N/Nitrite-N		
Unchlorinated	Cool to 4°C	48 hours
chlorinated	Cool to 4°C	14 days
combined	conc. H_2SO_4 pH < 2	28 days
o-Phosphate-P	Cool to 4°C	48 hours
Sulfate	Cool to 4°C	28 days
Perchlorate	Cool to 4°C	28 days
PCBSA	Cool to 4°C	28 days

8.3 The method of preservation and the holding time for samples analyzed by this method are determined by the anions of interest. In a given sample, the anion that requires the most preservation treatment and the shortest holding time will determine the preservation treatment. It is recommended that all samples be cooled to 4-C and held no longer than 28 days for Method A or Method C.

9. Calibration and Standardization
(See Standard Logs for recipes of all standards.)

9.1. Establish ion chromatographic operating parameters equivalent to those indicated in Table 1A or 1B.

9.2. For each analyte of interest, prepare calibration standards at a minimum of three concentration levels (five for method C) by adding accurately measured volumes of one or more stock standards (7.5) to a volumetric flask and diluting to volume with reagent water. The curve is forced through the 0 point. An acceptable curve has a $r^2 \geq 0.995$. A method blank is analyzed after the calibration to verify this point (d). If a sample analyte concentration exceeds the calibration range the sample may be diluted to fall within the range. If this is not possible then three new calibration

concentrations must be chosen, two of which must bracket the concentration of the sample analyte of interest. Each attenuation range of the instrument used to analyze a sample must be calibrated individually.

9.3. Using injections of 0.1 to 1.0 mL (determined by injection loop volume) of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded.

9.4. The calibration curve must be verified on each working day, or whenever the anion eluent is changed, and after every 20 samples. If the response or retention time for any analyte varies from the expected values by more than the range indicated under CCV standards, the test must be repeated, using fresh calibration standards. If the results are still out of range, a new calibration curve must be prepared for that analyte.

ICV Standards

	Analyte	Conc.	Acceptance Range %
Method A:			
	Cl	150ppm	90-110
	NO_3	111ppm	90-110
	SO_4	250ppm	90-110
	F	2ppm	90-110
	NO_2	2ppm	90-110
	PO_4	2ppm	90-110
Method C:	ClO_4	25ppb	90-110

CCV Standards

	Analyte	Conc. Mid	Conc. High	Acceptance Range %
Method A:				
	Cl	10	150ppm	90-110
	NO_3	44.3	111ppm	90-110
	SO_4	30	250ppm	90-110
	F	0.5	2.0ppm	90-110
	NO_2	0.5	2.0ppm	90-110

	PO_4	0.5	2.0ppm	90-110
Method C:	ClO_4	125	250ppb	90-110

Calibration Standards

Method A:

Std #1

Cl	1ppm	F	0.05ppm
NO_3	1ppm	NO_2	0.05 ppm
SO_4	1ppm	PO_4	0.05 ppm

Std #2

Cl	10ppm	F	0.1ppm
NO_3	25ppm	NO_2	0.1 ppm
SO_4	30ppm	PO_4	0.1 ppm

Std #3

Cl	20ppm	F	0.5ppm
NO_3	50ppm	NO_2	0.5 ppm
SO_4	60ppm	PO_4	0.5 ppm

Std #4

Cl	100ppm	F	1.0ppm
NO_3	150ppm	NO_2	1.0ppm
SO_4	150ppm	PO_4	1.0ppm

Std #5

Cl	200ppm	F	2.0ppm
NO_3	200ppm	NO_2	2.0ppm
SO_4	350ppm	PO_4	2.0ppm

Std #6

Cl	250ppm	F	5.0ppm
NO_3	250ppm	NO_2	5.0ppm
SO_4	400ppm	PO_4	5.0ppm

PCBSA Std #1 1ppm, Std #2 5ppm, Std #3 10ppm
Std #4 50ppm, Std #5 100ppm

Method C:

ClO_4: Std #1 4ppb, Std #2 10ppb, Std #3 50ppb
Std #4 100ppb, Std #5 250ppb

Lab Controls

Method A:

Acceptance range 90% - 110%

Cl	High	150 ppm	Low	10ppm
NO_3	High	111 ppm	Low	44.3ppm
SO_4	High	250 ppm	Low	30ppm
F	High	2.0 ppm	Low	0.5ppm
NO_2	High	2.0 ppm	Low	0.5ppm
PO_4	High	2.0 ppm	Low	0.5ppm

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PCBSA 25ppm Acceptance range 80% - 120%

Method C:

Acceptance range 80% - 120% (e)
ClO4 25ppb

Matrix Spikes

Method A: No spikes analyzed (f). Duplicates are analyzed instead since these analytes are rarely none detected.

Method C:

Acceptance range: waters 80% - 120% max RPD 20
Soils 75% - 125% max RPD 35

ClO4 12.5ppb X any prep or dilution factor

10. Quality Control

10.1. Our laboratory has a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability (10.2) and the analysis of control samples as a continuing check on performance. The laboratory maintains performance records to define and document the quality of data that are generated.

10.1.1. In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 10.2.

10.1.2. 5 to 10% of all samples are run in duplicate.

10.2. Before performing any analyses, the analyst demonstrates the ability to generate acceptable accuracy and precision with this method using a laboratory performance standard. Each analyst will analyze four replicates of a standard that is ten times their most recently proven MDL. Method C perchlorate requires four replicates at 25ppb. The acceptance criteria for this study is 90 – 110% recovery for water matrices and 80 – 120% recovery for solid matrices (g).

10.3. The laboratory develops and maintains accuracy statements of laboratory performance for each matrix being analyzed by the laboratory

10.4. Before processing any samples, the analyst demonstrates through the analysis of an aliquot of D.I. water (MB) that all glassware and reagent interferences are under control. Each time there is a change in reagents, the MB is monitored for the appearance of negative peaks as a safeguard against laboratory contamination (h).

10.5. When doubt exists over the identification of a peak in the chromatogram, confirmatory techniques such as sample dilution and fortification must be used.

10.6. Quality control check samples are analyzed concurrently with those performance evaluation sample studies required to maintain state certification.

10.7. For Method C (i), the linear calibration range is verified every 6 months or whenever a significant change in the instrument response is observed.

10.8. In order to verify that standards have been prepared correctly a LCS is performed using a standard of known concentration from an independent source. This laboratory control sample containing each analyte of concern is analyzed with each batch of samples processed. If more than 20 samples are run in a batch analyze one LCS for every 20 samples (10 for drinking water). Evaluate the accuracy by comparing to laboratory acceptance criteria. If acceptable data cannot be obtained, locate the problem and correct it. If during the course of a run a LCS is out of range, if possible it is rerun on the spot. If this is not possible the analyst may reevaluate the data based on peak height rather than peak area. If the data still does not fall within the acceptance criteria, the analyst may choose to use the six point calibration curve (for method A) to interpret the data rather than the three point lower level curve. If all the LCS' are in range under these conditions, the data is accepted. Otherwise a fresh calibration is performed and all samples are rerun starting from the last acceptable LCS.

11. Procedure

11.1. Set-up:

11.1.1. Prepare Eluant. Turn He valve to 5psi for method A and 30 psi for Method C. Check that the He line is connected to the eluant bottle. Set pump rate as per table 1.

11.1.2. On peaknet program – click on run icon. Under file click on load method. Method A – anion 300; Method C – a-clo4.met.
11.1.3. Wait for conductivity and pressure to stabilize.

11.2. Standardization and Calibration:
11.2.1. Using a clean syringe, fill one vial with the Method Blank.
11.2.1.1. Place vial in position #1 of autosampler.
11.2.1.2. Press <START> enter.
11.2.1.3. Init V <1> enter.
11.2.1.4. Rinse <0> enter.
11.2.1.5. Last V <1> enter.

11.2.2. Using a clean syringe, fill one vial with an initial calibration verification standard.
11.2.2.1. Place vial in position #2 of autosampler.
11.2.2.2. Press <START> enter.
11.2.2.3. Init V <1> enter.
11.2.2.4. Rinse <0> enter.
11.2.2.5. Last V <2> enter.
11.2.3. The initial calibration verification standard should read within the established control limits. If it does not, reinject it, if it still does not work, recalibrate.
11.2.3.1. Load calibration standards on the autosampler
11.2.3.2. Inject six calibration standards.
11.2.4. Check an initial calibration verification standard again.

11.3. Analysis:
11.3.1. Fill vials with sample, filtering (for Method A) through a 0.2 μm disc filter. For methods B & C, samples containing suspended material may be centrifuged or decanted.
11.3.2. Start the autosampler on vial 1 through 64.
11.3.2.1. Press <START> enter.
11.3.2.2. Init V <1> enter.
11.3.2.3. Rinse <0> enter.
11.3.2.4. Last V < # of last vial> enter.
Note: for method C, 2 vials per sample are loaded onto the autosampler.
11.3.3. Run continuing calibration verification standards every 10 samples. Run a lab control, method blank, and duplicate every 20 samples. Run matrix spikes every 20 samples for method B and C. Run a check standard at the end.
11.3.4. If a sample is above the high standard, dilute with D.I. water, according to the thickness and height of the peak. Make sure the peaknet software is calculating appropriately by observing peak heights and retention times.

11.4. Shutdown
11.4.1. Under Run – load stop method.
11.4.2. Turn pressure valve to 0 psi.

Note: Tables 1A and 1B summarize the recommended operating conditions for the ion chromatograph. Included in this table are estimated retention times that can be achieved by this method. Other columns, chromatographic conditions, or detectors may be used if the requirements of Section 10.2 are met.

11.5. Check system calibration daily and, if required, recalibrate as described in Section 9.

11.6. Load and inject a fixed amount of well mixed sample. Flush injection loop thoroughly, using each new sample. Use the same size loop for standards and samples. Record the resulting peak size in area or peak height units. An automated constant volume injection system may also be used.

11.7. The computer software comes with default retention time window widths. This is used to make identifications unless experience shows that the window requires adjustment (j). The experience of the analyst weighs heavily in the interpretation of chromatograms.

11.8. If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

11.9. If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, fortify the sample with an appropriate amount of standard and reanalyze.

Note: Retention time is inversely proportional to concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases this peak migration may produce poor resolution or identification.

11.10. The following extraction should be used for solid materials. Add an amount of reagent water equal to ten times the weight of dry solid material taken as a sample. This mixture is agitated for sixty minutes by shaking intermittently. Filter the resulting slurry before injecting using a 0.45 micron membrane type filter. With the exception of method C, this can be the type that attaches directly to the end of the syringe. Two samples per batch are spiked prior to extraction. These spikes are used to demonstrate that good recovery and identification of peaks is obtained with the users matrix.

12. Calculation

12.1. Prepare separate calibration curves for each anion of interest by plotting peak size in area, or peak height units of standards against concentration values. The system will then compute sample concentration by comparing sample peak response with the standard curve.

12.2. Report results in mg/L.

12.3. Report:
NO_2- as N
NO_3- as N or as NO_3 if desired by the client
$H(PO_4)_2$- as P

13. Precision and Accuracy - Method Detection Limit

13.1. The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1A and 1B were obtained using reagent waters.

14. Calculations associated with this method:

14.1. Total Anions (TA)
mequiv. of OH + CO3 + HCO3 + SO4 + Cl + NO3 = TA

14.2. Electrochemical Balance (ECB)
Total Cations (TC) – Total Anions (TA)

14.3. Total Dissolved Solids by Summation (TDSSUM)
mg/L of 0.6(Total Alkalinity) + Na + K + Ca + Mg + SO4 + Cl + NO3 + F + SiO3 = TDSSUM

Table 1A. Chromatographic Conditions and Detection Limits In Reagent Water (Method A)

Analyte	Peak #	MDL (mg/L)
Fluoride	1	0.01
Chloride	2	0.792
Bromide	4	0.0015
Nitrate-N	5	0.0115
o-Phosphate-P	6	0.003
Sulfate	7	0.028
PCBSA	8	<1 (EDL)

Standard Conditions:

Unit:	DX 120
Columns:	as specified in 6.2.2.1
Detector:	as specified in 6.2.4
Pump Rate:	2.0 mL/min.
Eluent:	as specified in 7.3.1
Sample Loop:	25 uL

Table 1B. Chromatographic Conditions and Detection Limits In Reagent Water (Method C)

Analyte	MDL (mg/L)
Perchlorate	0.0018

Standard Conditions:

Unit:	DX500
Column:	as specified in 6.2.2.3
Detector:	as specified in 6.2.4
Pump Rate:	1.0 mL/min.
Eluent:	as specified in 7.3
Sample Loop:	740 uL

15.0 Corrective Action For Out of Control Or Unacceptable Data:

See SOP Q06 – Corrective Action

16.0 Pollution Prevention and Waste Management:

See SOP S05 – Neutralization Procedure for Acid and Alkaline Wastes
SOP S07 – Pollution Prevention

Method Variations

(a). Low Level Check Frequency EPA Method 300.0 section 10.8.
(b). Low Level Check Duplicates EPA Method 300.0 section 10.9.
(c). Stability of Standards - EPA Method 300.0 section 7.5.

(d). Blank in Calibration – EPA Method 300.0 section 9.2. and DHS-IC-Rev 0 section 10.2.
(e) LCS Acceptance Limit - California Department of Health Services IC Rev 0, section 9.3.2, 9.3.3.
(f). Laboratory Fortified Sample Matrix required for each method – EPA Method 300.0 revision 2.1, section 9.4.1.
(g) .Demonstration of Capability EPA Method 300.0 section 10.2.
(h). Reagent Water Monitoring EPA Method 300.0 section 10.5.
(i). Proof of Linear Calibration Range required for each method - EPA Method 300.0 revision 2.1, section 9.2.2.
(j). Retention Time Window – EPA Method 300.0 section 11.4.

References:

EPA SW846 method 9056

EPA Methods for the Determination of Inorganic Substances in Environmental Samples, Method 300.

California Department of Health Services IC Rev 0

Approved by Susann K Thomas 8/25/00

METHOD #: EPA 350.1, SM 4500-NH_3 H

TITLE: I53 Nitrogen, Ammonia (Colorimetric, Automated Phenate)

ANALYTE: Ammonia Nitrogen

1.0 Scope and Application

1.1 This method covers the determination of ammonia in drinking, surface, and saline waters, domestic and industrial wastes in the range of 0.1 to 5.0 mg/L NH3 as N. This range is for photometric measurements made at 630nm in a 10 mm tubular flow cell. Higher concentrations can be determined by sample dilution.

2.0 Summary of Method

2.1 Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The blue color formed is intensified with sodium nitroprusside.

3.0 Sample Handling and Preservation

3.1 Preservation by addition of conc. H_2SO_4 to a pH < 2 and refrigeration at 4-C.

3.2 Safety: Safety glasses and gloves should be worn when dealing with acids and bases.

4.0 Interferences

4.1 Calcium and magnesium ions may be present in concentrations sufficient to cause precipitation problems during analysis. A 5% EDTA solution is used to prevent the precipitation of calcium and magnesium ions from river water and industrial waste. For sea water a sodium potassium tartrate solution may be used.

4.2 Sample turbidity and color may interfere with this method. Turbidity must be removed by filtration prior to analysis. Sample color that absorbs in the photometric range used will also interfere. Sample is diluted if necessary

4.3 Marked variation in acidity and alkalinity are eliminated by sample preservation with H_2SO_4. The pH is then checked to ensure that it is <2. (a) Due to the reducing nature of this environment, residual chlorine is not expected to be a problem. (b) The sample is neutralized prior to analysis by the addition of the first reagent which is a NaOH buffer. (c)

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5.0 Apparatus

5.1 Test tube rack from Lachat.

5.2 13 x 100 mm disposable culture tubes.

5.3 Lachat Quikchem Analyzer

5.4 Whatman 2 and Whatman 4 (11.0 cm) filter paper or Gelmin 0.45 micron disk filters.

5.5 100 ml beakers.

5.6 1 ml, 2 ml, 5 ml, and 10 ml pipets.

5.7 25 ml, 50 ml, and 100 ml graduated cylinders.

5.8 Helium Gas (technical grade).

5.7 Digestion hot plates

6.0 Reagents (d)

6.1 Nanopure water

6.2 Carrier or preserved water: 2ml of Sulfuric acid dilute to 1 gallon with Nanopure. Degas with Helium just prior to analysis.

6.3 Sodium phenolate: Using a 1 liter Erlenmeyer flask, 88ml of 88% phenol in 500 mL of Nanopure water. In small increments, cautiously add with agitation, 32 g of NaOH. Periodically cool flask under water faucet. When cool, dilute to 1 liter with Nanopure water.

6.4 Sodium hypochlorite solution: Dilute 250 mL of a bleach solution containing 5.25% NaOCl (such as "Clorox") to 500 mL with Nanopure water. Available chlorine level should approximate 2 to 3%. Since "Clorox" is a proprietary product, its formulation is subject to change. The analyst must remain alert to detecting any variation in this product significant to its use in this procedure. Due to the instability of this product, storage over an extended period should be avoided.

6.5 Buffer: Disodium ethylenediamine-tetraacetate (EDTA) (5%): Dissolve 50 g of EDTA (disodium salt) and 9g of NaOH in 1 liter of Nanopure water. Degas with Helium just prior to analysis.

6.6 Sodium nitroprusside (0.05%): Dissolve 3.5 g of sodium nitroprusside in 1 liter of Nanopure water.

7.0 Standards:

7.1 Lab Control Sample (LCS) and Matrix Spikes (MS/MSD):

7.1.1 Stock Solution: EM 1000 mg/L NH_3 Standard.

7.1.2 LCS: Dilute 1 ml of stock to 1000 ml in a volumetric flask with preserved water (7.3). The concentration is 1 mg/L NH_3 or 0.78 mg/L NH_3-N

7.1.3 Acceptability: The result of the LCS analysis is compared to statistically generated acceptance ranges. If the analysis does not fall within the acceptance range,(85%-115%) the analysis is stopped until the cause is determined and the LCS is within the acceptance range.

7.2 Matrix Spike (MS) / Matrix Spike Duplicate (MSD)

7.2.1 Spike solution: Use a 1:1 dilution of a sample and LCS. Mix well.
7.2.2 Acceptability: 70%-130%, RPD maximum 20

7.3 Method Blank

7.3.2 Use carrier from section 6.2
7.3.3 Acceptability: MB must read below RL of 0.1mg/L

Note: Since the intensity of the color used to quantify the concentration is pH dependent, the acid concentration of the carrier and the standard ammonia solutions should approximate that of the samples.

7.4 Calibration Standard:
7.4.1 Stock Ammonia Standard:
7.4.1.1 Dehydrate Ammonium Chloride (NH_4Cl) in a 105°C oven.
7.4.1.2 Allow to cool in a dessicator. Weigh out 3.819 g NH4Cl.
7.4.1.3 Dilute to 1 liter with nanopure water in a volumetric flask.
7.4.1.4 Pour the solution into a 1 liter amber bottle. Keep out of sunlight.
7.4.2 Use the stock NH_3-N standard for the calibration standards (1000ppm).

7.4.3 Dilute 5 ml of stock standard to 1000 ml with preserved water. This will be the 5.0 mg/L working standard and the intermediate standard.

7.4.4 Dilute from the intermediate standard for the other working standards as follows:

7.4.4.1 2.5 mg/L standard: 50 ml of 5.0 mg/L diluted to 100 mL with preserved water.

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7.4.4.2 1.0 mg/L standard: 20 mL of 5.0 mg/L diluted to 100 mL with preserved water.
7.4.4.3 0.2 mg/L standard: 4 mL of 5.0 mg/L diluted to 100 mL with preserved water.
7.4.4.4 0.05 mg/L standard: 1 mL of 5.0 mg/L diluted to 100 mL with preserved water

8.0 Procedure:

8.1 Preserve samples with H_2SO_4 to a pH of <2.

8.2 Rinse all glassware with 1:1 HCl.

8.3 Use the following volumes based on sample matrix:

8.3.1 Industrial or Influent Wastewater – 2-5mL.

8.3.2 Effluent Wastewater – 25-50 mL.

8.3.3 Well water - 50 ml.

8.3.4 Solid – Make a 1:10 water extract, extract and swirl periodically for one hour.

8.4 Dilute all samples to a final volume of 50 ml. If less than 5 ml of sample is used, dilute with carrier otherwise Nanopure water may be used.

Note: Filter all samples. Distillation is not required since computability data on representative samples is being generated to show that this step is not necessary however manual distillation will be required to resolve ant controversies (e).

8.5 Pour samples into test tubes in the test tube rack. Analyze on the lachat.

8.6 If diluted samples read below 0.1 mg/L, re-analyze using more sample and diluting to a final volume of 50 ml.

8.7 If any sample reads above 5.0 mg/L, re-analyze using less sample.

8.8 Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding Nanopure water through sample line.

8.9 Arrange ammonia standards in sampler. Complete loading of sampler tray with unknown samples.

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8.10 See Lachat SOP I41 for general operating instructions.

8.11 Choose method: NH4PHE

8.12 After system has stabilized with water only running through the lines and the heater temperature has reached at least 58° C, put the reagent tube into the carrier bottle.

8.13 Wait until carrier has reached the end of the board before putting the buffer tube into the reagent bottle.

8.14 Continue on in this manner, adding all of the reagents in the order in which they are numbered.

8.15 Once the baseline is stable and the temperature of the heater has returned to 58-62°C, calibration may begin.

8.16 When an acceptable calibration has been performed, submit the tray of samples.

9.0 Calculations

9.1 Prepare appropriate standard curve derived from processing ammonia standards through manifold. Compute concentration of samples by comparing sample peak areas (f) with standard curve.

9.2 Apply dilution factors to samples where less than 50ml was anlalyzed.

9.3 The reporting limit is 0.1mg/L.

9.4 Report 2 significant figures.

9.5 Inorganic Nitrogen = $NH_3N + NO_3N + NO_2N$

10.0 Definitions: See SOP Q15 – SOP Definitions

11.0 Safety: The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. A reference file of material data handling sheets is made available to all personnel involved in the chemical analysis.

See SOP S01 – Concentrated Acids and Bases
SOP S02 – Compressed Gas Cylinder Handling
SOP S03 – Spill Control Policy

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12.0 Corrective Action For Out of Control Or Unacceptable Data:
See SOP Q06 – Corrective Action

13.0 Pollution Prevention and Waste Management:
See SOP S05 – Neutralization Procedure for Acid and Alkaline Wastes
SOP S06 – Disposal of Chlorinated Solvents
SOP S07 – Pollution Prevention

Method Variations

(a) Elimination of Marked Acidity or Alkalinity – Standard Methods 18th Edition 4500-NH_3 H 1b.
(b) Chlorine Pretreatment – Standard Methods 18th Edition 4500-NH_3 A 2
(c) Sample Neutralization – Standard Methods 18th Edition 4500-NH_3 A 3
(d) Reagent Recipes –Lachat Quikchem Methods NH3 Phenolate Method 10-107-06-1-B © 3/13/98 and Standard Methods 20th Edition 4500-NH_3
(e) Distillation – 40 Code of Federal Regulations part 136.
(f) Quantification Using Peak Area– Standard Methods 18th Edition 4500-NH_3 H 5

References:

Standard Methods for the Examination of Water and Wastewater APHA, AWWA, WPCF 18th Edition.

Lachat Quikchem Methods 10-107-06-2-E © 3/21/91

EPA Method 350.1 Methods for the Chemical Analysis of Waters and Wastes.

Approved by Susan K Thomas 7/10/00

8 ATTACHMENTS

8.1 ATTACHMENT A: CLEANING OF EQUIPMENT FOR WATER SAMPLING

8.2 ATTACHMENT B: STANDARD OPERATION PROCEDURES